

# STUDY OF VANADIUM EMISSION CONTROL IN COMBUSTION SYSTEMS BY THERMODYNAMIC EQUILIBRIUM ANALYSES

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## INTRODUCTION

Toxic metal emissions from combustion sources such as vanadium are of great concerns. It is concentrated in certain types of coal, heavy oil and petroleum coke<sup>1,2</sup>. Once emitted, it can be transported to distance, resulting in adverse environmental and health effects<sup>3</sup>. It is known that vanadium may cause cardiovascular disease, bronchitis and lung carcinoma. Due to its high concentration, interest has been developed to recover vanadium from ash<sup>4</sup>. Vanadium, as other metals in the fuel matrix, may enter the gas stream in combustion systems by vaporization or entrainment of vanadium compounds. At high temperatures, it undergoes various chemical reactions to form various species depending on the combustion environment and composition in the system. At the cooler post combustion zone, various aerosol dynamics proceed resulting in the transformation of vanadium into particulate phase. The particle size distribution depends on the temperature history and the existing species in the system<sup>5</sup>. A lot of research studies have shown that metals undergoing this pathway generally form aerosols in the submicrometer regime. Unfortunately, traditional control devices have their minimum efficiency in this size regime. Thus, it is important to develop new techniques to effectively control vanadium emission.

Recently, studies have been conducted to use mineral sorbents to capture heavy metals. Heavy metals are chemically adsorbed on the injected sorbent particles. As these sorbent particles are relatively larger in size (typically greater than 10  $\mu\text{m}$ ), the metal-sorbent particles can be easily collected using traditional particulate control devices. Shadman and co-workers<sup>6,7</sup> used silica, alumina and various naturally available materials (i.e. bauxite, kaolinite and lime) to capture lead and cadmium. Venkatesh et al.<sup>8</sup> evaluated various mineral sorbents constituting a spectrum of aluminosilicate compounds for immobilization of several heavy metals. Biswas and co-workers<sup>9-11</sup> *in-situ* generated sorbents particles with very high surface area to capture lead and mercury. However, no study using sorbents to capture vanadium has been conducted.

At high temperatures, reactions are fast and equilibrium can possibly be achieved. Hence thermodynamic equilibrium methods can be applied to determine the potential sorbent materials. The objective of this study is to use equilibrium calculations to determine the effective materials that can chemically adsorb vanadium. Optimal conditions to achieve high efficiencies will be determined. The impact of various common constituents in combustion systems on the performance will be assessed. The most effective one for vanadium control will be determined.

## METHODOLOGY

A computer code, STANJAN<sup>12</sup>, was used to implement the calculations. Its principle is to minimize the system's Gibbs free energy by using the method of elemental potentials combined with atom constraints. The thermodynamic data for all the relevant species were obtained from the literature<sup>13,14</sup>. Table 1 lists the species that are included in the calculations. The simulation conditions are listed in Table 2. The concentrations correspond to the levels found in a typical coal combustion system<sup>15</sup>. Due to the lack of coal's thermodynamic data, methane ( $\text{CH}_4$ ) is used in the calculations. As the metal concentration is trace in the fuel, the form of the fuel used in the system does not affect the metal's speciation.

Calculations were first conducted to determine the behavior of vanadium in a typical combustion system without sorbent as the baseline. The performance of individual sorbent was then investigated for a wide range of temperatures. Parametric analyses were then conducted to evaluate the impact of chlorine and sulfur. Finally, all the sorbents were included and competition for vanadium among the various sorbents was placed to determine the best sorbent.

Table 1. List of Species used in the Equilibrium Calculation

Reactant	Product
V	V, $\text{VCl}_2$ , $\text{VCl}_3$ , $\text{VCl}_4$ , VO, $\text{VO}_2$ , $\text{VOCl}_3$ , $\text{V}_2\text{C}$ , $\text{VCl}_4$ , $\text{V}_2\text{O}_3$ , $\text{V}_2\text{O}_4$ , $\text{V}_2\text{O}_5$ , V(g), $\text{VCl}_2(\text{g})$ , $\text{VCl}_4(\text{g})$ , $\text{VO}(\text{g})$ , $\text{VOCl}_3(\text{g})$ , $\text{VO}_2(\text{g})$
Ca	$\text{CaCl}_2$ , CaO, $\text{CaO}_2$ , $\text{CaSO}_3$ , $\text{CaSO}_4$ , CaS, $\text{CaCO}_3$ , $\text{Ca}(\text{VO}_3)_2$ , $\text{Ca}_2\text{V}_2\text{O}_7$ , $\text{Ca}_3(\text{VO}_4)_2$ , Ca(g), $\text{CaCl}_2(\text{g})$ , CaS(g)
Mg	Mg, $\text{Mg}(\text{OH})_2$ , $\text{MgCO}_3$ , $\text{MgCl}_2$ , MgO, $\text{MgSO}_4$ , $\text{Mg}(\text{VO}_3)_2$ , $\text{Mg}_2\text{V}_2\text{O}_7$ , Mg(g), $\text{MgCl}_2(\text{g})$ , $\text{MgOH}(\text{g})$
Na	Na, NaCl, NaOH, $\text{NaClO}_4$ , $\text{NaHCO}_3$ , $\text{Na}_2\text{CO}_3$ , $\text{Na}_2\text{O}$ , $\text{Na}_2\text{O}_2$ , $\text{Na}_2\text{SO}_3$ , $\text{Na}_2\text{SO}_4$ , $\text{NaVO}_3$ , $\text{Na}_3\text{VO}_4$ , $\text{Na}_4\text{V}_2\text{O}_7$ , Na(g), NaCl(g), NaOH(g), $\text{Na}_2\text{O}_2\text{H}_2(\text{g})$ , $\text{Na}_2\text{SO}_4(\text{g})$
Common compound	$\text{CH}_4$ , CO, $\text{CO}_2$ , Cl, HCl, HOCl, NOCl, ClO, $\text{Cl}_2$ , H, OH, $\text{H}_2\text{O}$ , N, NO, $\text{NO}_2$ , $\text{N}_2$ , $\text{N}_2\text{O}$ , $\text{O}_2$ , S, $\text{SO}_2$ , $\text{SO}_3$

Table 2. Simulation conditions for evaluating the performance of various sorbents in capturing vanadium (unit: mole).

Set.	V	Cl	S	CH <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub>	Na <sub>2</sub> O	CaCO <sub>3</sub>	MgO
I-1	$7 \times 10^{-7}$	0	0	1	4	15	0	0	0
I-2	$7 \times 10^{-7}$	0.011	0	1	4	15	0	0	0
II-1	$7 \times 10^{-7}$	0	0	1	4	15	$4.12 \times 10^{-4}$	0	0
II-2	$7 \times 10^{-7}$	0	0	1	4	15	0	0.0034	0
II-3	$7 \times 10^{-7}$	0	0	1	4	15	0	0	$9.95 \times 10^{-4}$
III-1	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	$4.12 \times 10^{-4}$	0	0
III-2	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	0.0778	0	0
III-3	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	0.0934	0	0
III-4	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	0	0.0034	0
III-5	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	0	0.0389	0
III-6	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	0	0.0467	0
III-7	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	0	0	$9.95 \times 10^{-4}$
III-8	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	0	0	0.0389
III-9	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	0	0	0.0467
IV-1	$7 \times 10^{-7}$	0	0	1	4	15	0.0389	0.0389	0.0389
IV-2	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	$4.12 \times 10^{-4}$	0.0034	$9.95 \times 10^{-4}$
IV-3	$7 \times 10^{-7}$	0.011	0.0389	1	4	15	0.0389	0.0389	0.0389

## RESULTS AND DISCUSSIONS

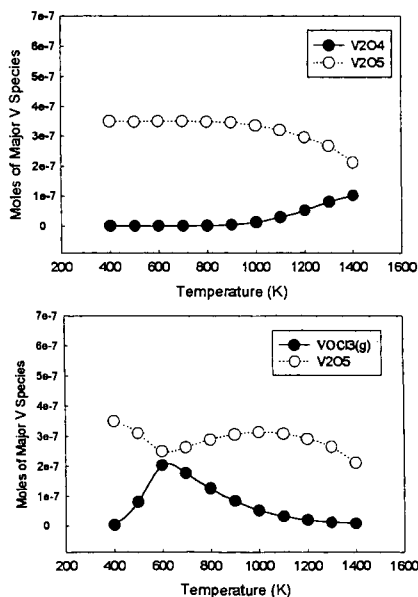
### Set I: Vanadium in a Typical Coal Combustion System Without Sorbents Added.

In the first set, the behavior of vanadium in a typical combustion system is studied. The results are shown in Figure 1. As shown, the major product is divanadium pentaoxide ( $V_2O_5$ ) over the entire range studied. Metal oxide aerosols formed in combustion systems are generally in the submicrometer range and hence they are not desired.<sup>17</sup>

Figure 1 Partition of vanadium speciation in a typical coal combustion system without chlorine

Chlorine is known to have a strong affinity to react with many metals. Therefore, its effect on vanadium speciation is also studied. The results are shown in Figure 2. As shown, vanadium oxytrichloride ( $VOCl_3$ ) is important at medium temperatures (~500 – 1000 K) although not dominant. Compared with earlier studies on other heavy metals<sup>5</sup>, chlorine's affinity to react with vanadium is relatively weak. Hence, it is probable that the presence of chlorine in typical combustion systems will not significantly affect vanadium's speciation.

Figure 2 Partition of Vanadium species in a typical coal combustion system with chlorine



Although sulfur has been reported to be important for certain metals<sup>5,16</sup>, calculations were not conducted in this study as there is no thermodynamic data available for vanadium-sulfur compounds.

### Set II. Performance of Individual Sorbent.

Next, individual sorbent is examined for its performance. The amount of each sorbent used corresponds to the level found in typical coal. The results are shown in Figures 3a – 3c. As shown, all the sorbent materials used are very effective in almost the entire temperature range (forming sorbent-vanadium products). This indicates the high potential of using these materials. However, it should be noted that it does not necessarily guarantee the success of the process because of the influence by other constituents in the system. This will be discussed more in the next section.

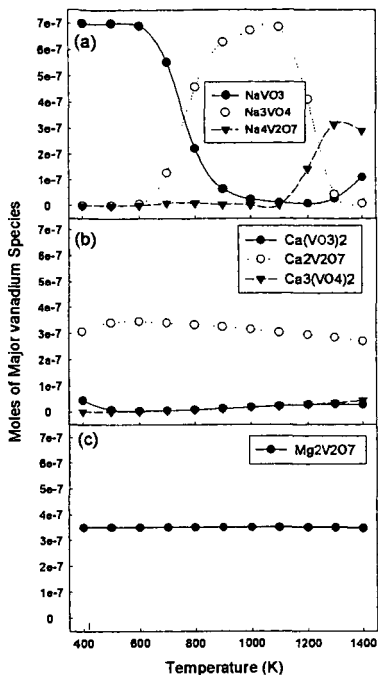


Figure 3 Partition of vanadium species using: (a) Na-based sorbent; (b) Ca-based (b) sorbent; (c) Mg-based sorbent

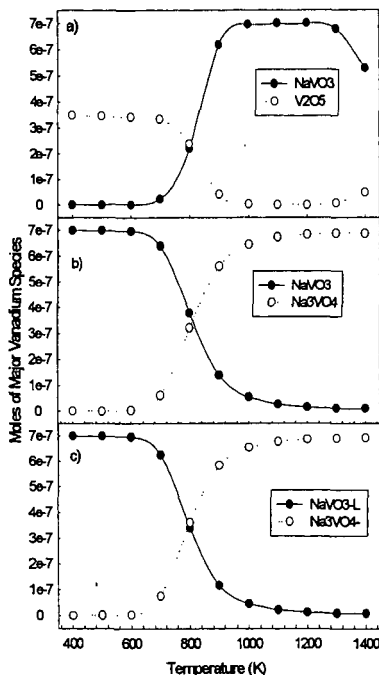


Figure 4 Impact of chlorine and sulfur on the effectiveness of Na-based sorbent: a) typical concentration in coal; b) stoichiometric amount of sorbent; c) to react with Cl and S 20% excess of sorbent than the stoichiometric amount

### Set III Effects of Chlorine and Sulfur on the Performance of the Various Sorbent Used

Chlorine and sulfur are very common in coal and other fuels. They may react with vanadium to form vanadium chloride or sulfate. They can also react with the sorbent materials, for example, calcium sulfate (gypsum), thus reducing the available amount of sorbents to react with vanadium. Hence, their impact is investigated. First, calculations were performed using their concentrations in typical coal (Table 3). Then the stoichiometric amount necessary for scrubbing sulfur was used. Finally, 20% more of the sorbent than the stoichiometric amount was used. The results are shown in Figures 4 – 6 for Na-, Ca-, and Mg-based sorbent respectively.

#### Na-based sorbent

Figure 4a shows that  $V_2O_5$  is dominant at lower temperatures ( $< 800K$ ), indicating the ineffectiveness of the process. Examination of the products shows that the majority of sodium forms sodium sulfate ( $Na_2SO_4$ ), thus depleting the available sodium. When  $Na_2SO_4$  becomes unstable at higher temperatures ( $> 900K$ ), the sorbent is available again to react with vanadium. When the amount of sorbent is enough to deplete sulfur and chlorine, this process is effective (forming vanadium sorbent compound) even at lower temperatures, as shown in Figures 4b when stoichiometric amount of sorbent reacting with chlorine and sulfur is used.

#### Ca-based sorbent

Similar to the sodium case, Ca-based sorbent is ineffective at lower temperatures ( $< 1000K$ , Figure 5a).  $V_2O_5$  is the dominant species and the cause is the same. When stoichiometric amount of calcium sorbent is used (Figure 5b), the temperature range for effective vanadium capture expands but  $V_2O_5$  is still not captured effectively when the temperature is lower than 800 K. Only when excess sorbent is used (Figure 5c), calcium vanadate becomes the dominant species.

#### Mg-based sorbent

The similar trend is observed when Mg-based sorbent is used. However, Mg-based sorbent seems to be less effective than the other two sorbents investigated. As shown in Figure 5a, magnesium vanadates are not present even at high temperatures. The reason is due to magnesium's high affinity to form magnesium sulfate even at high temperatures. Magnesium vanadate becomes dominant only when excess amount of sorbent is used as shown in Figure 6c.

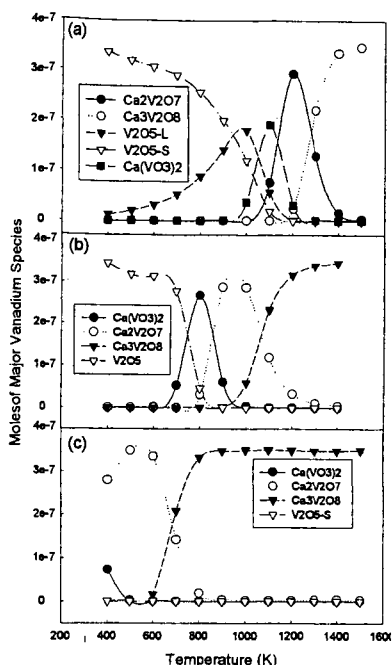


Figure 5 Impact of chlorine and sulfur on the effectiveness of Ca-based sorbent: a) typical concentration in coal; b) stoichiometric amount of sorbent to react with chlorine and sulfate; c) 20% excess of sorbent then the stoichiometric amount

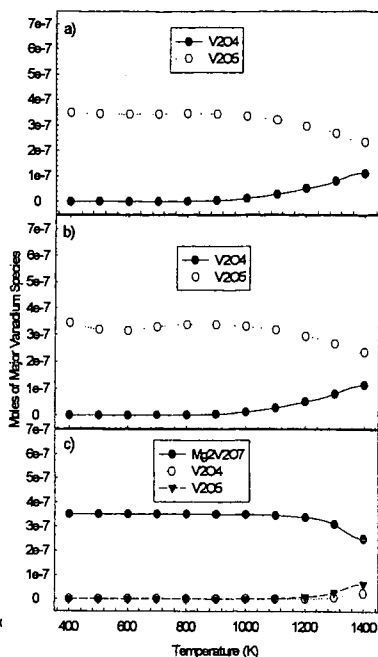


Figure 6 Impact of chlorine and sulfur on the effectiveness of Mg-based sorbent: a) typical concentration in coal; b) stoichiometric amount of sorbent to react with chlorine and sulfate; c) 20% excess of sorbent then the stoichiometric amount

#### Set IV : Determination of the most effective sorbent.

To determine the most effective sorbent, in the final set of calculations all the sorbents were included. Calculations were first conducted for typical coal combustion assuming no chlorine or sulfur. Chlorine and sulfur concentrations in typical coal were then used. Finally, stoichiometric amounts of sorbent materials were used. The results are shown in Figures 7a-c, respectively.

Without chlorine or sulfur in the system, Na- based sorbent apparently is the most effective one in the entire temperature range investigated (Figure 7a). However, it has a stronger affinity to react with chlorine and sulfur. Hence, it becomes ineffective when chlorine or sulfur is present. On the other hand calcium is not significantly affected by the presence of chlorine. It is impaired by sulfur only at lower temperatures. Hence, Ca-based sorbent is more competent when chlorine or sulfur is present (Figure 7b). When stoichiometric amounts of sorbents are used, Ca- based sorbent is effective even at lower temperatures. This is probably due to the shielding effects of the presence of Na- and Mg- based sorbents as they are more vulnerable to chlorine and sulfur.

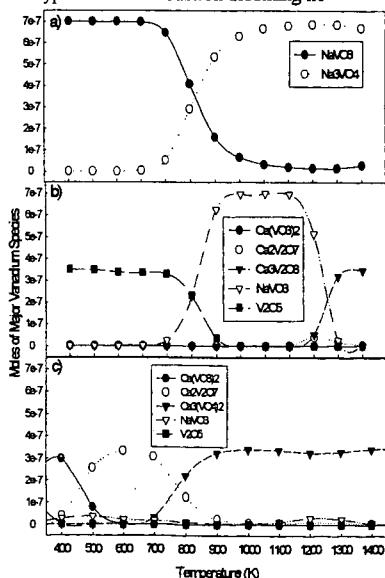


Figure 7 Partition of vanadium species when various amount of all sorbents are used: a) no chlorine and sulfate; b) typical coal combustion; c) stoichiometric amount of sorbents

## CONCLUSIONS

Vanadium is concentrated in various fuels and the emission of vanadium from combustion systems is of concern. Mineral sorbents have been demonstrated to be effective to control various toxic metals in combustion systems. In this study, equilibrium calculations were conducted to identify the potential sorbent materials to chemically adsorb vanadium. Na-, Ca- and Mg-based sorbents were found to be effective. However, the presence of chlorine and sulfur in the system may affect the performance of these sorbents. Na-based sorbent is significantly impaired when chlorine or sulfur is present. Sodium chloride and sulfate are formed under this condition. Ca- and Mg-based sorbents are less affected by chlorine but sulfur substantially reduces their performance. Sulfates are formed under this condition. The formation of sulfates or chlorides diminishes the available sorbents for vanadium capture. Calculations were also performed to determine the most effective sorbent. Na-based sorbent is found to be the most effective one when no chlorine or sulfur is present. However, Ca-based sorbent becomes the most robust one when chlorine or sulfur exists.

This study provides the insight of the reactions between vanadium and sorbents as well as the impact of various operating conditions. The information obtained can be used as a basis for developing a better strategy for managing vanadium emission problems.

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